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Eugene E. Haller, Pearl P. Li, G. Scott Hubbard
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October 1978

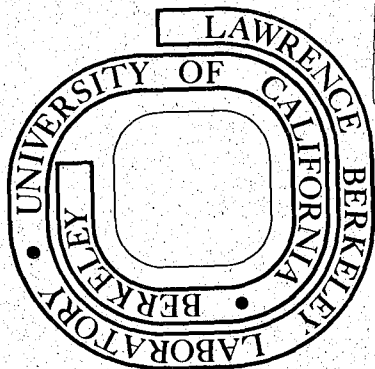
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Eugene E. Haller, Pearl P. Li, G. Scott Hubbard and William L. Hansen

Abstract

Deep Level Transient Spectroscopy (DLTS)⁵ has been applied for the first time to high-purity germanium p-i-n diodes. Using the correlator technique,⁶ a large number of peaks due to acceptor levels in the forbidden band have been observed. The levels due to substitutional copper, to copper-hydrogen complexes and to divacancy-hydrogen defects have been positively identified. Several unknown levels have been discovered. The results obtained with DLTS are in excellent agreement with results from Hall-effect measurements. DLTS is the perfect tool to follow the creation and annealing of radiation defects.

Introduction

Impurities, point and line defects can introduce energy levels in the forbidden band of a semiconductor. If the levels are close to one of the band-edges they are called "shallow" (i.e. ~ 10 meV in Ge; ~ 40 meV in Si). Their concentration determines the width of the depletion layer of a reverse biased diode at a given voltage. If the energy levels do not lie close to either band-edge they are called "deep". Such levels can retain free charge carriers (electrons/holes) for prolonged times. Deep levels are often called "traps". The presence of a small concentration is detrimental to the performance of semiconductor p-n or p-i-n radiation or particle detectors since retention of 10⁻⁴ of the charge produced by an ionizing event can lead to an unsymmetric line-shape in a spectrum. Therefore, much effort has been spent in the characterization and in the removal of trapping centers from semiconductor crystals.

From the analysis of the shape of gamma-ray photopeaks, one can draw certain conclusions about traps in a p-i-n detector.^{1,2} However, this approach is very indirect and a large number of additional parameters besides the traps influence the photopeak line shapes. More quantitative answers can be obtained from Hall Effect measurements on single crystals.^{3,4} This method works well for trap depths up to about one-third of the band gap. Levels close to or in the middle of the band gap are hidden by the generation of intrinsic carriers. Furthermore, in the presence of several trap levels with similar energies, it becomes very difficult to obtain accurate values for trap concentration and position. A further disadvantage of the Hall Effect method is that it does not work for the actual detector diode but only for unprocessed single crystal samples. Since the detector processing may introduce impurities, this is a significant disadvantage of the Hall Effect method.

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Deep-Level Transient Spectroscopy, DLTS

The Deep-Level Transient Spectroscopy (DLTS) method was introduced by Lang⁵ in 1974. This kind of spectroscopy uses the strong dependence of the emission rate of carriers from deep traps on temperature and on the energy of the trap. Deep traps are periodically filled by a pulsed bias reduction across a reverse biased junction (p-n or p-i-n). Figure 1 shows the change of the bias and capacitance with time. In the presence of traps, a slow recovery of the capacitive value occurs after the pulse. Figure 2 displays the condition of the depletion layer inside a n⁺-p-p⁺ device at the different times shown in Fig. 1. The depletion layer is shaded in each case. Capacity change in period # 3 to 4 occurs because the deep levels (in our example deep acceptors, i.e. majority traps) do not get filled with electrons instantaneously when the full bias is reapplied. The filling proceeds exponentially with time. The time constant τ depends on the trap energy E (E = energy of the trap level measured from the corresponding bandedge) and the temperature T:

$$\tau = C_0 T^{-2} \exp\left(\frac{E}{kT}\right) \quad (1)$$

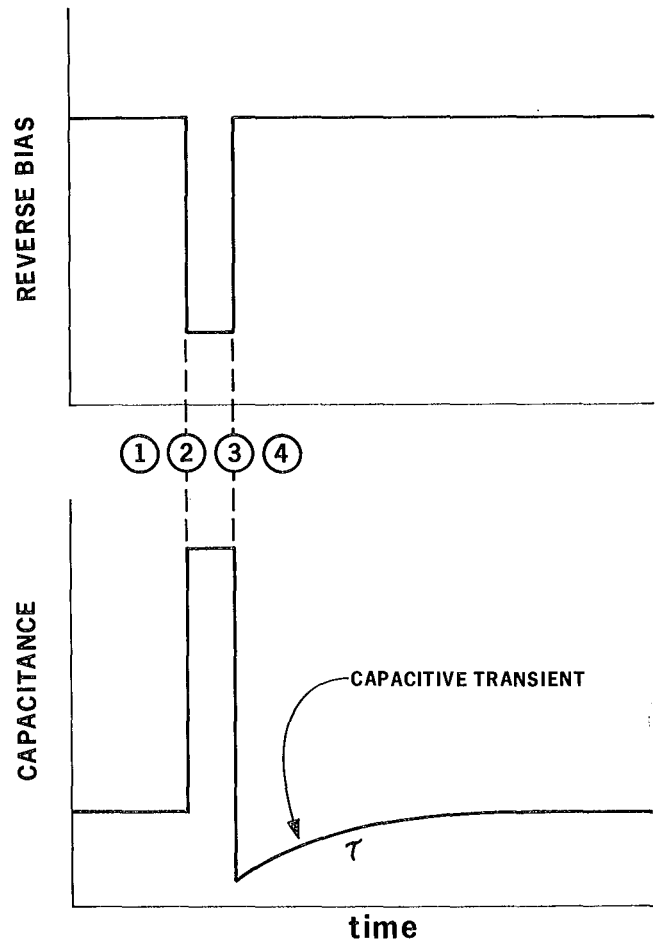
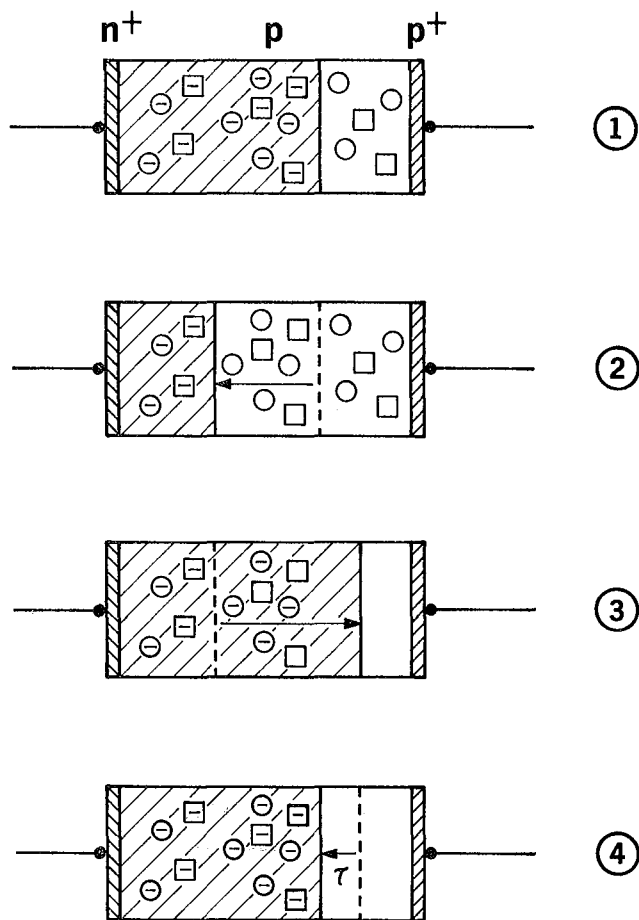


Fig. 1 Time dependence of bias and of capacitance of a partially depleted p-n or p-i-n semiconductor junction in a Deep Level Transient Spectrometer.



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Fig. 2 Change of the depletion layer and the charge state of shallow (circles) and deep (squares) acceptors in a p-i-n device. Shallow acceptors follow the bias changes given instantaneously while the deep traps get refilled much more slowly with a time constant τ .

where C_0 is a constant and k is the Boltzman constant ($= .08633 \text{ meV K}^{-1}$). The emission rate e is the inverse of τ :

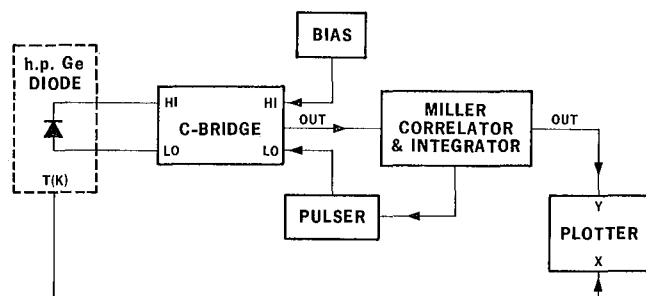
$$e = C_1 T^2 \exp\left(-\frac{E}{kT}\right) \quad (2)$$

Various schemes have been used to measure the capacitive transient and its recovery time constant. The correlator technique employed by Miller⁶ uses the fact that the best signal to noise ratio can be obtained if the filtering function has the same time dependence as the signal. We have used the correlator technique for our measurements.

Experimental

A block diagram of the electronics of our Deep Level Transient Spectrometer is shown in Fig. 3. The diode under test is mounted inside a variable temperature cryostat. A Stirling engine cryocooler which reaches a minimum temperature of 28 K with room temperature water cooling and about 22 K with precooled methanol cooling is used. Great care is taken to avoid all light leaks to the detector. The temperature

DEEP LEVEL TRANSIENT SPECTROMETER



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Fig. 3 Block diagram of a simple Deep Level Transient Spectrometer.

is measured by a forward biased silicon diode.⁷ The capacitance of the test diode is continuously measured with a 1 MHz bridge.⁸ A variable DC-bias is applied through the HI-lead of the bridge and the bias reduction pulse is fed through the LO-lead to the diode. In a few cases, a IR-light emitting diode next to the diode under test is used to change the charge state of present traps. The output signal of the capacitance bridge is fed to the Miller correlator where it is weighed by an exponentially decaying waveform with a time constant τ_r that can be set to values between 1 and 100 ms. The product is integrated and drives the Y-axis of a plotter. The X-axis is directly connected to the temperature measurement diode. The correlator output is a maximum when the time constants of signal and weighting function τ_r are equal. This happens at a well defined temperature for each trap (Eq. 1). We have used five time constants τ_r (1.3, 3, 10, 30 and 100 ms) to determine E and C_1 of each trap.

Results

A large number of high-purity germanium diodes have been studied. Most of the devices were standard diodes of the kind used for gamma and X-ray or particle detection (area $\sim 10 \text{ cm}^2$, thickness $\sim .5 \text{ cm}$). The internal time-constant due to the resistance of the undepleted material and the capacitance of the depletion layer is always made smaller than the inverse of the C-bridge measurement frequency. In some cases (very high-purity), the diodes had to be made thinner than standard ($<.5 \text{ cm}$) to satisfy this requirement.

The first diodes measured contained well known traps. Three crystals grown in vacuum, a nitrogen atmosphere and a hydrogen atmosphere were copper doped by diffusion from a surface source. Figure 4 shows the DLT spectra of the three diodes made from these crystals. Peak 4 is due to the doubly ionized copper acceptor (Cu^{2-}). Peaks 1 and 3 are due to copper-hydrogen complex acceptors. The origin of peak 2 is unknown. It shows up in all crystals containing oxygen concentrations $\geq 5 \times 10^{13} \text{ cm}^{-3}$. The emission rate parameters are compiled in Table 1. Next we investigated

Table 1

Peak No.	C_1	E(meV)	Impurity Correlation
1	5.2×10^7	60.4	copper, hydrogen
2	1.6×10^6	68.7	oxygen
3	2.3×10^7	179.5	copper, hydrogen
4	2.3×10^8	300	copper, doubly ionized acceptor (Cu^{++})
5	} not identified		
6			
7	3.6×10^7	67.4	divancy-hydrogen, singly ionized acceptor
8	} not identified		
9			
10	6.7×10^7	151.8	copper, lithium, hydrogen
11	--	--	minority carrier trap; copper, triply ionized acceptor (Cu^{+++}).

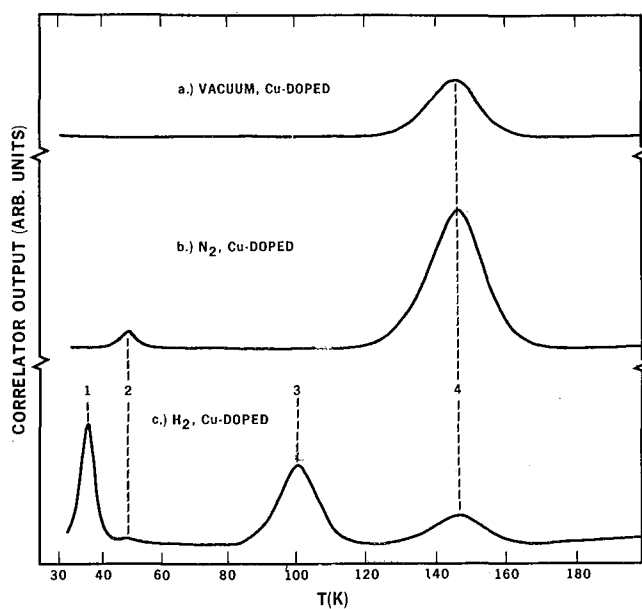
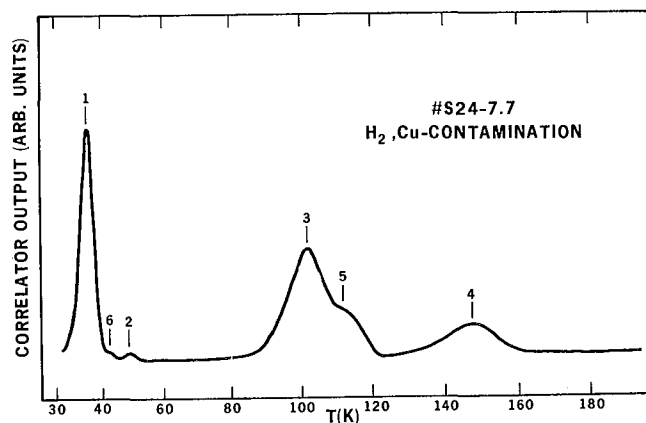


Fig. 4 DLT spectra of three high-purity germanium diodes which were intentionally doped with copper.

two diodes which exhibited trapping (Figs. 5 and 7). In diode S24-7.7 (Fig. 5) all copper and oxygen related peaks (1-4) are clearly visible. Two further peaks 5 and 6 have not been identified. The same diode produces the DLT spectrum shown in Fig. 6 when a light pulse instead of a bias reduction is used to change the charge state of the traps. A new negative peak 11 is present. We assume that peak 11 is due to the triply ionized copper acceptor (Cu^{+++}).

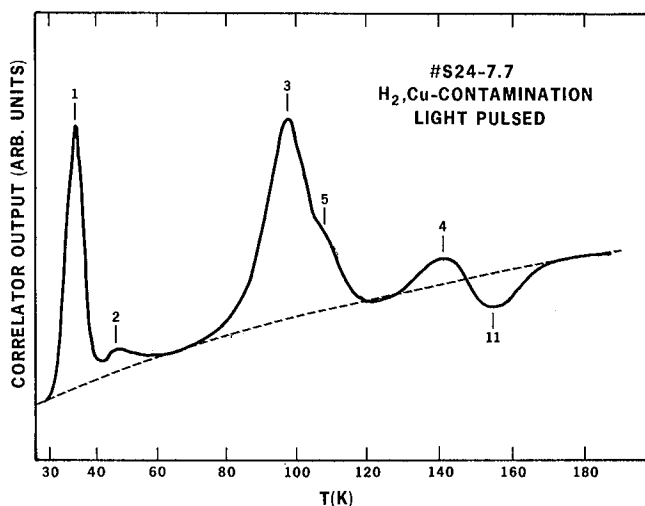


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Fig. 5 DLT spectrum of diode S24-7.7. Peaks 1, 3 and 5 clearly indicate the presence of copper.

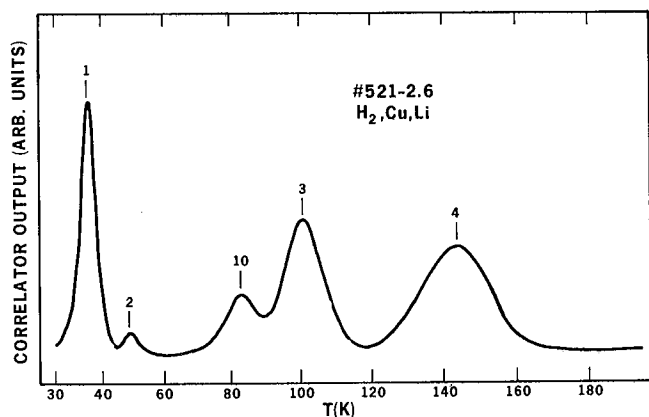
Diode 521-2.6 exhibits all copper and oxygen related peaks (Fig. 7). A new peak 10 is present. This diode has a very deeply diffused lithium n^+ -contact. We correlate peak 10 with a lithium-copper acceptor. There is no doubt that detectors S24-7.7 and 521-2.6 contain copper, and it is most probable that the various copper related acceptors are the source of trapping.

Dislocation free germanium contains the well known divacancy-hydrogen complex.⁹ A diode made from dislocation free material exhibits a very pronounced peak around 43 K (Fig. 8). The energy determined from Hall effect measurements and from DLTS are in good agreement. To caution future DLT spectroscopists, we include DLT spectra of the very pure n-type diode 475-1.5. Different surface treatment or contamination produces a series of peaks (Fig. 9). These peaks are due to surface states. This result suggests the use of grounded guard-ring structures for these measurements. Such devices would allow the separate study of bulk and surface levels.



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Fig. 6 Same diode as in Fig. 5 but light instead of bias pulses are changing the charge state of deep traps. A minority trap produces a negative peak 11.

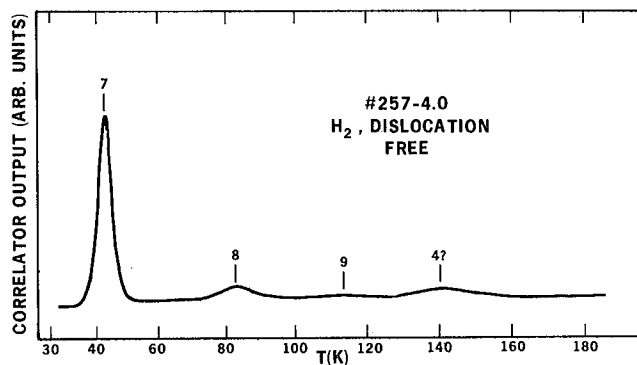


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Fig. 7 DLT spectrum of diode 521-2.6. The Li-n⁺-contact was diffused for prolonged times. Peak 10 is most probably due to a lithium-copper complex. All peaks characteristic for copper are clearly present (peaks 1, 3 and 4).

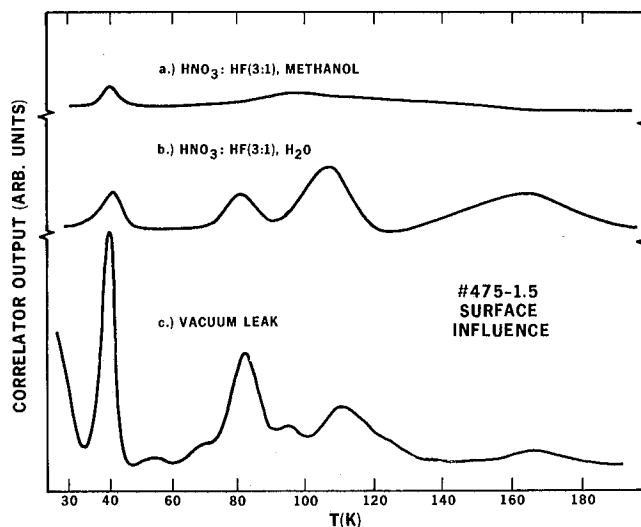
Discussion and Conclusions

It is not the goal of this paper to present a complete study of a large number of deep levels in high-purity germanium. Our intention is to demonstrate how powerful DLT spectroscopy is and what kind of studies can be undertaken. From our experiments, which deal exclusively with majority traps in n⁺-p-p⁺ diodes, it becomes clear that the method is very sensitive and selective. Both levels in the germanium bulk and at the surface can produce DLTS peaks. We foresee the possibility of using this new spectroscopy for the identification of surface contaminants and pollution studies. Experiments to evaluate the use of very pure Ge detectors as fast neutron integrating flux monitors are in progress. It is known that the defects



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Fig. 8 Diode 257-4.0 is made from dislocation free high-purity germanium. Peak 7 is due to the divancy-hydrogen complex. Spurious peaks 8 and 9 have not been identified.



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Fig. 9 DLT spectra of the same n-type high-purity germanium diode 475-1.5. Different surface conditions lead to a number of peaks.

produced by the fast neutrons create deep levels in the germanium. If these levels are not too broadly spread in the forbidden band, it should be possible to obtain a rather sensitive fast neutron monitor. With the new possibility to determine the energy and concentration of deep traps in high-purity Ge, it will be possible to predict the performance of large volume gamma-ray detectors.

Acknowledgments

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